

# (12) UK Patent Application (19) GB (11) 2 289 466 (13) A

(43) Date of A Publication 22.11.1995

(21) Application No 9409312.7

(22) Date of Filing 10.05.1994

(71) Applicant(s)

**Dytech Corporation Limited**

**(Incorporated in the United Kingdom)**

**Stopes Road, Stannington, SHEFFIELD, S6 6BY,  
United Kingdom**

(72) Inventor(s)

**Rodney Martin Sambrook  
Robert Terence Smith**

(74) Agent and/or Address for Service

**Laurence Shaw  
5th Floor, Metropolitan House, 1 Hagley Road,  
Edgbaston, BIRMINGHAM, B16 8TG, United Kingdom**

(51) INT CL<sup>6</sup>

**C04B 38/10 , C08J 9/04**

(52) UK CL (Edition N )

**C3C C101 C157 C180 C375 C520 C522  
U1S S1385 S1462**

(56) Documents Cited

**WO 93/04013 A**

(58) Field of Search

**UK CL (Edition M ) C1J , C3C  
INT CL<sup>5</sup> C04B , C08J  
Online databases : WPI**

(54) Porous ceramic articles

(57) A gas generating substance is added to an aqueous dispersion containing ceramic particles and a polymerisable monomer. The gas generating substance forms gas bubbles under the influence of the exotherm of polymerisation, and the pressure and/or temperature are adjusted so that the substance generates the gas before or during the initial stages of the polymerisation.

GB 2 289 466 A

## PRODUCTION OF POROUS ARTICLES

The invention relates to the production of porous articles and is an improvement in or modification of the invention disclosed in our patent application PCT/GB92/01493 published under number WO 93/04103 on March 4, 1993. All of the disclosure of that specification is hereby incorporated herein.

The method described and claimed in the earlier application comprises the step of forming a dispersion comprising particles of refractory material in a liquid carrier, introducing gas into the dispersion and removing the liquid carrier to provide a solid article having pores derived from the bubbles of gas, characterised by controlling the critical viscosity of the dispersion to be from about 5 mPa.s, (the level below which the entrapped gas bubbles will tend to escape), to about 1000 mPa.s, (the level above which the entrapped gas bubbles cannot be introduced). The critical viscosity is preferably from about 20 mPa.s to about 250 mPa.s. After the gas is introduced the liquid carrier is removed, typically water is driven off by heat.

One optional step is the inclusion of a polymerisable monomer to have an effect when the liquid carrier is removed. Soluble acrylates and acrylamides are given as suitable additives and they are polymerised by the use of catalysts and/or heat.

There may be a need in certain circumstances for a porous article in which the pores are highly interconnected. This invention is based on the appreciation that by carrying out foaming in a defined way such articles or articles having another predetermined structure of pores can readily be formed.

According to the invention in one aspect there is provided a method of making a porous refractory article, the method comprising the steps of:

- forming an aqueous dispersion of ceramic particles including a polymerisable monomer component which on polymerisation generates an exotherm
- adding a thermally decomposable gas generating substance
- adding agents such as initiator and/or catalyst to cause the polymerisation
- adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.

Preferably the reaction is carried out under reduced pressure, say about 60 mm Hg.

The thermally decomposable gas generating substance will, under the appropriate conditions, generate the gas in situ. The temperature at which the gas is generated depends on the substance in question, and the overall conditions, e.g. temperature and pressure. The substance is preferably one which after decomposition leaves no residues which in the context tend to contaminate, decomposes at a pH of between about 7.5 and 9, and does not generate free oxygen which would inhibit polymerisation. Preferred are ammonium carbonate, ammonium bicarbonate, ammonium carbamate; and the like. Metallic carbonates can also be used where the presence of the residual metal oxide will have no adverse effect.

It is an aspect of this invention that by controlling the temperature and pressure the decomposition rate of the gas generating substance is controlled. The foaming reaction could then be triggered by the increase in temperature associated with the onset of polymerisation. This triggering process requires control over the slurry temperature and pressure prior to the onset of polymerisation and the use of a catalyst. Alternatively the slurry could be stored at a predetermined pressure and temperature and microwave energy can be used to induce polymerisation and the decomposition of the gas generating substance.

The ceramic particles can be derived from a wide variety of materials such as metals, metallic oxides, non-metallic ceramics and cermets. Examples, given for illustration and not limitation, include alumina, cordierite, magnesia, mullite, silica, silicon carbide, silicon nitride, tungsten nitride, zirconia; and the like.

In one optional step, foaming is carried out at atmospheric pressure using ammonium carbonate or the like as the gas generating substance by using an initiator which induces polymerisation at a temperature higher than that at which ammonium persulphate operates. Such initiators are well known. The initiator would be selected by type and concentration to delay the onset of polymerisation until after the foaming agent had decomposed at 60°C at atmospheric pressure. In another option, the composition contains ammonium persulphate or the like as initiator and the foaming agent is one which decomposes at a temperature lower than that at which the persulphate decomposes. Such agents are well known, e.g. volatile liquids, gases, and halogenated hydrocarbons.

In order that the invention may be well understood it will now be described by way of illustration with reference to the following examples.

**Exempl I**

Alumina (70g) , a premix solution (21.27g) comprising ammonium acrylate 29.1%, methylene bisacrylamide 0.9% and the remainder water, and dispersants comprising ammonium salts of polyacrylate solution (1g) and polymethacrylate (2g), were mixed with deionized water (5g) to form a homogeneous slurry. An amount of foaming agent (ammonium bicarbonate) was then mixed with the slurry and allowed to dissolve. This was followed by the addition of initiator (ammonium persulphate) and finally the foam stabilising agent (surfactant - Triton X-100). The prepared slurry was then transferred to a microwave oven and heated to between 70 - 80°C in under one minute to dissolve the ammonium carbonate.

Various tests were conducted adjusting the microwave power setting and the initiator and foaming agent concentrations. The initiator concentrations were varied between 0.3 and 0.075g per sample. The foaming agent concentration (ammonium carbonate) was varied between 1g and 3g per sample. It was found that the addition of the foaming agent did not interfere with the quality of the ceramic slurry. The ammonium carbonate crystals mixed in the slurry tended to settle to the bottom of the container. During the application of microwaves, the crystals in the bottom of the container tended to decompose when the temperature approached 60°C and created a gas pocket at the bottom of the container. The ammonium carbonate dissolved within the slurry decomposed to create small gas bubbles which grew and became interconnected with increasing temperature. After foam production the foamed samples were dried at room temperature for 1 day and then at 60°C for 1 day. This was then followed by sintering at 1550°C for 2 h. Table I shows the green and sintered densities obtained in the case of some samples.

## Example II

Alumina, premix solution and dispersants were mixed as in Example I. The foaming agent (ammonium carbonate) was ground to a fine powder and mixed in the slurry. This was followed by the addition of initiator (ammonium persulphate) 1.2g. The foam stabilising agent (surfactant) was then mixed with the slurry and finally a small amount of catalyst (tetraethylmethylethelenediamine) 0.05 ml was added. The slurry was transferred to a vacuum desiccator at room temperature. At a reduced pressure of about 60 mm of mercury, the slurry started to decompose which resulted in it foaming. This behaviour was quite unexpected and it seems that the ammonium carbonate was decomposing and generating gas.

With the onset of polymerisation the foam expanded even further as the temperature of the gas increased. This required the pressure within the vacuum chamber to be increased to compensate for the expanding foam. After a few minutes polymerisation was complete and the pressure within the chamber was brought back up to atmospheric and the polymerised foam removed from the chamber. The result was a ceramic foam with an extremely open pore structure and low density. The foamed samples were dried at room temperature for 1 day and then at 60°C for 1 day. This was then followed by sintering at 1550°C for 2 h. Table II shows the green and sintered density obtained for one sample.

**TABLE I**

<b>SAMPLE</b>	<b>GREEN DENSITY</b>	<b>SINTERED DENSITY</b>
1	0.55	0.86
2	0.62	0.97
3	0.41	0.64

**TABLE II**

1	0.19	0.29
---	------	------

**CLAIMS**

1. A method of making a porous ceramic article, the method comprising the steps of:
  - forming an aqueous dispersion of ceramic particles including a polymerisable monomer component which on polymerisation generates an exotherm
  - adding a thermally decomposable gas generating substance
  - adding agents such as initiator and/or catalyst to cause the polymerisation
  - agitating the dispersion containing the additives and adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.
2. A method according to Claim 1, wherein the thermally decomposable gas generating substance is ammonium carbonate, ammonium bicarbonate; ammonium carbamate; or the like.
3. A method according to Claim 1 or 2, including the step of triggering the foaming by heat energy.



4. A method according to Claim 3, wherein the heat energy is provided by the increase in temperature associated with the onset of polymerisation.
5. A method according to Claim 1, wherein an initiator such as ammonium persulphate is present, and the thermally decomposable gas generating substance decomposes at a temperature lower than that at which ammonium carbonate decomposes.
6. A method according to any preceding Claim, wherein the reaction is carried out under reduced pressure.
7. A method according to Claim 6 wherein the pressure is about 60 mm Hg.
8. A method according to any preceding Claim, including drying the ceramic article, and then subjecting it to sintering.

**Amendments to the claims have been filed as follows**

**CLAIMS**

1. A method of making a porous refractory article, the method comprising the steps of:
  - forming an aqueous dispersion of ceramic particles including a polymerisable monomer component which on polymerisation generates an exotherm
  - adding a thermally decomposable gas generating substance
  - adding agents such as initiator and/or catalyst to cause the polymerisation
  - adjusting the temperature and/or pressure so that the gas generating substance generates the gas before or during the initial stage of polymerisation of the monomer component whereby the gas forms bubbles which under the heat of the exotherm interconnect to form an interconnected open pore structure.
2. A method according to Claim 1, wherein the reaction is carried out under reduced pressure.
3. A method according to Claim 2, wherein the pressure is 60 mm Hg.
4. A method according to any preceding Claim, wherein the substance is one which after decomposition leaves no residues which in the context tend to contaminate, decomposes at a pH of between about 7.5 and 9, and does not generate free oxygen.

5. A method according to Claim 4, wherein the substance is ammonium carbonate, ammonium bicarbonate, ammonium carbamate; and the like.
6. A method according to any preceding Claim, wherein the temperature and pressure are controlled to control the decomposition rate of the gas generating substance.
7. A method according to any of Claim 1 to 6, wherein the dispersion is stored at a predetermined pressure and temperature and microwave energy is used to induce polymerisation and the decomposition of the gas generating substance.
8. A method according to any preceding Claim, wherein the ceramic particles are metals, metallic oxides, non-metallic ceramics and cermets.
9. A method according to any preceding Claim, wherein foaming is carried out at atmospheric pressure using ammonium carbonate or the like as the gas generating substance by using an initiator which induces polymerisation at a temperature higher than that at which ammonium persulphate operates.
10. A method according to any of Claims 1 to 9, wherein the dispersion contains ammonium persulphate or the like as initiator and the foaming agent is one which decomposes at a temperature lower than that at which the persulphate decomposes.
11. A method of making a porous article, substantially as described.

<b>Patents Act 1977</b> <b>Examiner's report to the Comptroller under Section 17</b> <b>(the Search report)</b>	<b>Application number</b> <b>GB 9409312.7</b>
<b>Relevant Technical Fields</b>  (i) UK Cl (Ed.M)      C3C, C1J (ii) Int Cl (Ed.5)      C08J, C04B  <b>Databases (see below)</b> (i) UK Patent Office collections of GB, EP, WO and US patent specifications.  (ii) ONLINE DATABASES: WPI	<b>Search Examiner</b> <b>M J PRICE</b>
	<b>Date of completion of Search</b> <b>9 AUGUST 1994</b>
	<b>Documents considered relevant following a search in respect of Claims :-</b> <b>1-8</b>

**Categories of documents**

<b>X:</b> Document indicating lack of novelty or of inventive step.	<b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.
<b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.	<b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.
<b>A:</b> Document indicating technological background and/or state of the art.	<b>&amp;:</b> Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	WO 93/04013 (DYTECH) note the correct publication number	

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).